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FRACTIONATION OF PHTHALIC RESINS, AND DETERMINATION

OF THE DISPERSIONS OF THEIR MOLECULAR WEIGHTS

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ABSTRACT: This article deals with the preparative fractionation
of domestically produced phthalic resins, determination of the
limit viscosity number of the separated fractions, and mathematical
and graphic estimation of the dispersion of the molecular weights
in order to secure data for a more detailed characterization of
the resins as coat-forming substances.

INTRODUCTION

Increasing demands imposed upon coat-forming substances as a basic component /821*

of materials serving to protect objects exposed to various sorts of destructive

action create a need for our becoming better acquainted with the structure of

these substances. In the literature devoted to problems having to do with the

production and testing of lacquer resins as substances capable of forming

coatings with a specific adhesion to the base, more and more space has been

occupied by studies on the link between the structure, the size, and the

polydispersity of the molecules on the one hand, and their properties in action

on the other hand. The ratios established have inclined some researchers

toward seeking a possibility of securing polymers having predetermined properties

through the course of changing the parameters of the synthesis and of fractioning

the products obtained.

The purpose of the present study was the preparative fractionation of

domestically produced phthalic resins, determination of the limit viscosity

number of the separated fractions, and mathematical and graphic estimation of

the dispersion of the molecular weights in order to secure data for a more

detailed characterization of the resins as coat-forming substances.

Among the known methods of separating the molecular weights of polymers,

it appears that the most useful laboratory method, for the case of phthalic

resins, is their precipitative fractionation from solutions. This is dictated

* Numbers in the margin indicate pagination in the foreign text.

by the simplicity of the method and by the need for subjecting the separated fractions to further analysis. This sort of method has been used in the studies of many investigators [1-5].

In the present study we have used the preparative method of fractionation applied by Ivanfi [5] and by Helme and Bosshard [3]. The fractionation is carried out on 10 - 15% solutions of the resin in acetone, the precipitating agent being water.

EXPERIMENTAL PART

Reagents and Apparatus

Acetone, pure

Benzene, pure d.a.

Methyl-ethyl ketone, pure d.a.

Capillary viscometer with suspended meniscus

Ultrathermostat having accuracy of ± 0.05° C

Stopwatch

Fractionation

Three phthalic resins - two of type L-61, and one of type R-39, produced by the Cieszyn Paint and Lacquer Factory, were subjected to preparative fractionation.

The L-61 resin came from two separate production series. This resin is produced through condensation of the mono- and di-glycerides of the fatty acids of linseed oil plus phthalic anhydride.

R-39 resin is a product of the condensation of castor oil, glycerine, and phthalic anhydride.

For fractionation, 15% solutions of the resins in acetone were prepared. Since these solutions contained suspensions of the insoluble constituents, they were filtered before fractionation by being run through G 3 porous glass filters. Then the solutions were transferred to a separator of 300 ml capacity having a short discharge. Water, introduced into the solution by means of a microburette, was used as a precipitating agent. The first portion of water is added until the solution first definitely becomes clouded. This solution is heated until the clouding disappears and is left until the strata separate.

The fraction secured is transferred to an evaporating dish, dried to constant weight, and then weighed.

In precipitating the subsequent fractions the quantity of water added is such that the entirety of the resin becomes divided into fractions having a similar quota by weight. In these studies we sought to achieve approximately equal numbers of fractions (about 10). The separated fraction was dried to constant weight at a temperature of 40° C in a vacuum drier.

Measurement of the Viscosity and Determination of the Limit Viscosity Number (LVN) of the Fractions Separated Out.

Measurement of the viscosity of the resin solutions was accomplished by making use of a modified Schneider capillary viscometer as specified in [6]. The viscosity of the resin solutions was designated by four concentrations: 0.06 g/ml, 0.045 g/ml, 0.030 g.ml, and 0.015 g.ml. In the case of the L-61 resin the solvent was benzene, whereas for the R-39 resin it was methyl-ethyl ketone. The use of a different solvent in the case of the R-39 resin was because of the anomalies which made their appearance in its benzene solutions. /823

The designation was carried out at a temperature of 20° C. In order to get this, the viscometer was placed in a thermostatically controlled bath.

The time it took the solvents and the solution to discharge from the calibrated part of the measurement vessel was determined. The measurement was repeated 3 - 5 times for each concentration of a solution.

The results of the measurements were not to differ among themselves by more than 0.3 seconds. The values secured from the measurements serve to evaluate reduced viscosities: $\eta_{zr} = \dfrac{\eta_{w1}}{C}$. The LVN of the fractions separated is indicated graphically by preparing a chart of the ratio $\dfrac{\eta_{w1}}{C} = f(C)$ and by interpolating for $C \to 0$. This ratio, having a linear character, is presented in Figure 1.

Interpretation and Discussion of Results

The polydispersity of large-molecule compounds can be expressed graphically through the integral and the differential curve of the distribution of weight. The integral curve represents the weight of the fractions of the polymer as

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a function of the molecular weight, whereas the differential curve expresses the percentage content of macromolecules having a particular molecular weight in the polymer under investigation. In this way Helme and Bosshard [3] interpreted the dispersion of molecular mass by using the results of molecular weight measurements of the phthalic resin fractions isolated by the precipitation method. Some investigators have asserted that there is a connection between the molecular weight and the limit viscosity number (LVN) of phthalic resins, for which reason the curves of distribution of mass may also be defined in relation to that value.
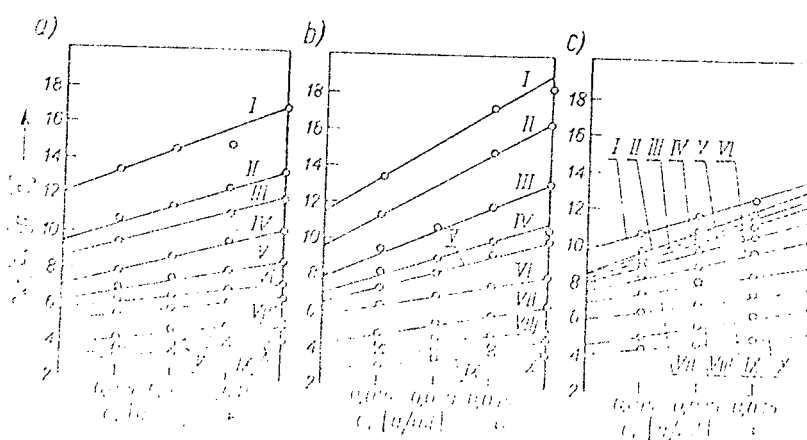

Figure 1. Reduced Viscosity and Limit Viscosity Number of Individual Solutions (I-X) of Resin Fractions: a - L-61 (I); b - L-61 (II); c - R-39.

These curves can be calculated from a Tung equation [7]:

$$I[\eta] = 1 - \exp\left(-a[\eta]^b\right)$$

where: $I[\eta]$ indicates the cumulative weight of the fraction,

$[\eta]$ is the limit viscosity number of the fraction,

$a - b$ are constants which can be indicated graphically be making a graph of the function $x_i = f(y_i)$ with $x_i = \lg[\eta]$,

$$y_i = \lg\left[\lg\frac{1}{1-I[\eta_i]} : \lg e\right]$$, or by the method of least squares.

Table 1 gives the data necessary for determining the values of the coefficients a and b.

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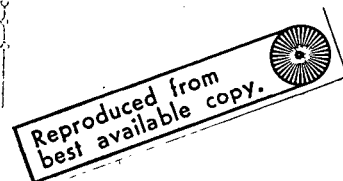
The straight lines shown in Figure 2 make it possible to define a as log a, a parameter giving a fixed value of y_i for $x_i =)$, and b as the coefficient of inclination of the straight line for $y_i = 0$. Figures 2-a and 2-b show straight lines illustrating the coefficients a and b graphically (solid lines) and, for the sake of comparison, by the method of least squares (broken lines).

On applying the method of least squares one observes that the values a and b are then correct if the equation

$$F(b \ \lg a) = \sum_{i=1}^{m} (bx_i + \lg a - y_i)^2$$

reaches a minimum.

This equation reaches a minimum if the partial derivative relative to b, or $\lg a$, become equal to zero, i.e., when

$$\frac{\partial F(b, \lg a)}{\partial \lg a} = 0$$

$$\frac{\partial F(b, \lg a)}{\partial b} = 0$$

After differentiation of the above equations and appropriate transformations, one gets the following expression defining the coefficients a and b:

$$b = \frac{\sum_{i=1}^{m} x_i y_i - \dfrac{\sum_{i=1}^{m} x_i \sum_{i=1}^{m} y_i}{m}}{\sum_{i=1}^{m} x_i^2 - \dfrac{\left(\sum_{i=1}^{m} x_i\right)^2}{m}}$$

$$\lg a = \frac{\sum_{i=1}^{m} y_i - b\left(\sum_{i=1}^{m} x_i\right)}{m}$$

In Table 2 we give the values of the coefficients a and b as obtained by the graphic method and by the method of least squares.

TABLE 1.   RESULTS OF INVESTIGATIONS ON INDIVIDUAL FRACTIONS OF THE RESINS INVESTIGATED.

| Fraction	Resin L-61 (I)			Resin L-61 (II)			Resin R-39		
	LVN (η) ml/g.	proportion of fraction by weight	comulative weight of fraction	LVN (η) ml/g.	proportion of fraction by weight	cumulative weight of fraction	LVN (η) ml/g.	proportion of fraction by weight	comulative weight of fraction
XI	---	---	---	2,80	0,0880	0,0880	---	---	---
X	2,85	0,0568	0,0568	3,45	0,0893	0,1773	4,10	0,1367	0,1367
IX	3,05	0,0802	0,1370	3,80	0,0895	0,2668	4,65	0,0955	0,2322
VIII	3,65	0,1163	0,2533	4,20	0,1150	0,3818	5,90	0,1067	0,3389
VII	4,65	0,0876	0,3409	5,65	0,1253	0,5081	6,85	0,1108	0,4497
VI	5,75	0,0632	0,4041	6,55	0,0757	0,5838	7,50	0,0820	0,5317
V	6,20	0,1002	0,5043	7,17	0,0687	0,6516	8,00	0,0797	0,6114
IV	7,00	0,1092	0,6135	7,95	0,0537	0,7053	8,05	0,0693	0,6807
III	8,60	0,1219	0,7354	8,17	0,0687	0,7740	8,20	0,0575	0,7382
II	9,50	0,0803	0,8157	9,70	0,0994	0,8734	8,50	0,1593	0,8975
I	12,15	0,1843	1,0000	11,65	0,1266	1,0000	9,80	0,1025	1,0000

(Commas indicate decimal points.)
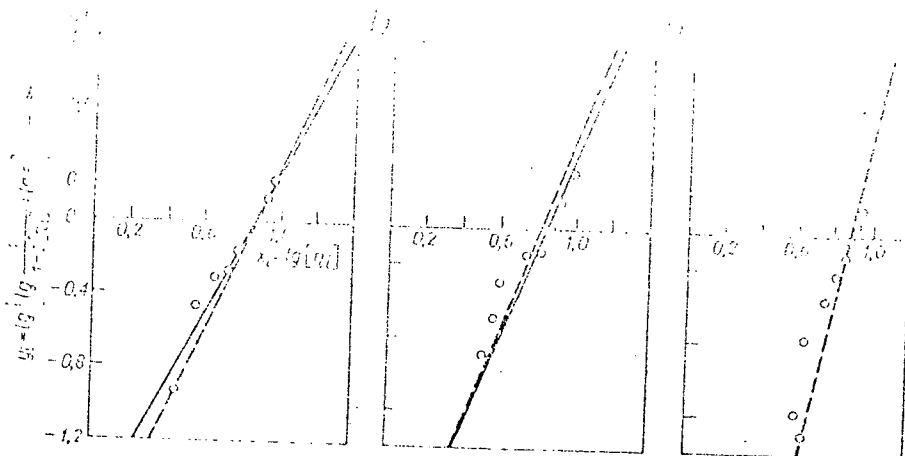
Figure 2. Straight Lines Indicating the Values of the Coefficients a and b in the Tung Equation. Solid lines are indicated graphically; broken lines are indicated by the method of least squares: a - resin L-61 (I); b - resin L-61 (II); c - resin R - 39.

TABLE 2. VALUES OF COEFFICIENTS a AND b IN THE TUNG EQUATION FOR THE RESINS UNDER INVESTIGATION.

Method of calculating coefficients	Value of coefficient a	Value of coefficient b
Graphic method		
a) resin L-61 (I)	0,0249	1,825
b) resin L-61 (II)	0,00933	2,31
Method of least squares		
a) resin L-61 (I)	0,0154	1,825
b) resin L-61 (II)	0,00771	2,593
c) resin R-39	0,000219	4,2593

(Commas indicate decimal points.)

Taking into account the computed and the graphically indicated coefficients of the distribution a and b respectively, the Tung equation is differentiated as follows:

$$\frac{dI([\eta])}{d[\eta]} = \frac{d}{d[\eta]}\,[1-\exp(-b[\eta]^{a})]$$

$$\frac{dI([\eta])}{d[\eta]} = \frac{a \cdot b[\eta]^{b-1}}{e^{a[\eta]b}}$$

Solving the differential equation in order to obtain the value of $\dfrac{dI([\eta])}{d[\eta]}$
calls for successive sustitution of the value [η] measured for individual fractions of the resin. The values $\dfrac{dI([\eta])}{d[\eta]}$ secured in this way can be presented, as a function of [η], as a differential curve in a system of coordinates.

A graphic presentation of the results achieved for the investigation of the resins is illustrated below in Figures 3-a, 3-b, and 3-c, which contain, together with differential curves, integral curves for the distribution of molecular mass, likewise expressed on the basis of a Tung equation in the form:

$$I([\eta]) = 1 - e^{-a[\eta]^b}$$

In the diagrams we give curves produced by the various methods of calculating the coefficients a and b of the Tung equation (Figures 3-a and 3-b). The distinct difference in the structure of these curves becomes most sharply pronounced as regards resin L-61 (I).
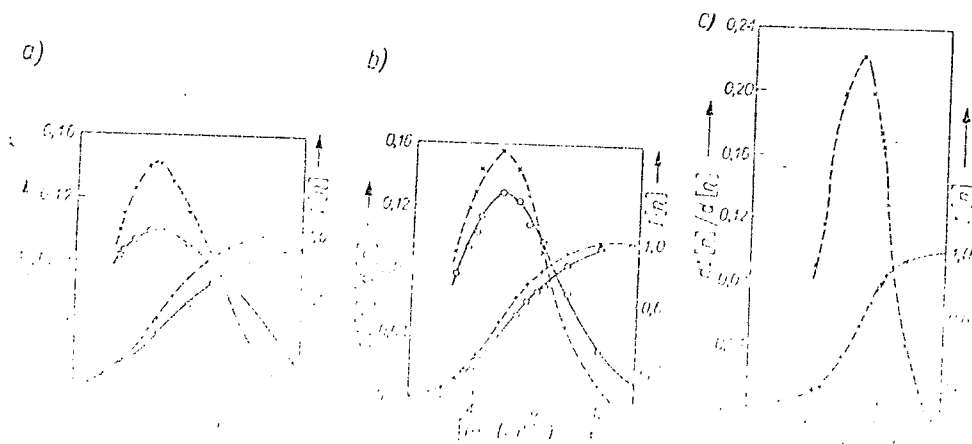
Figure 3. Integral and Differential Curves for the Dispersion of the Molecular Mass of the Resins Under Investigation. Solid lines are those defined when the coefficients a and b found graphically are used; broken lines are those calculated by the method of least squares: a - resin L-61 (I); b - resin L-61 (II); c - resin R-39.

It has been determined that the method of least squares makes possible the calculation of a more probable course of simple functions y = lg a + bx

than can be achieved through the graphic means of constructing straight lines defining the values of the coefficients a and b.

In this connection a discussion of the curves of dispersion of molecular mass, constructed on the basis of data secured through the mathematical method, has been carried out for the resins under investigation.

Analysis of the diagrams obtained enables us to assert that resins L-61 (I) and L-61 (II) (I and II designate different production series) are distinguished from each other to a slight extent in the dispersion of molecular mass. In the case of resin L-61 (I), 81% of the fractions lie below 8.3 LVN expressed in ml/g, which corresponds to 86% of the fractions of resin L-61 (II). The maximum $\frac{dI([\eta])}{d[\eta]}$ for the resins L-61 (I) and L-61 (II) in question is different and comes to 0.142 and 0.158, respectively.

This means that resin L-61 (II) has a very restricted dispersion of molecular mass.

The maximum value of the limit viscosity numbers is shifted; it is 5 ml/g for resin L-61 (I) and 5.6 ml/g for resin L-61 (II) which means that the mean molecular mass of resin L-61 (II) is greater than the corresponding value for resin L-61 (I).

The diagrams dealing with resin R-39 (3c) cannot be compared with resin L-61, because the calculated absolute values of the LVN have no common terms of reference. This is due to the fact that a different solvent was used in measuring viscosity. 90% of the fractions of this resin have a limit viscosity number within limit of 4 - 8.5 ml/g. The maximum of the differential curve comes to 0.223, which corresponds to a LVN of 6.6 ml/g. In addition, analysis of the diagrams of the functions $y = \lg a + b$ in Figure 2-a,b, and c makes possible a preliminary qualitative estimate of the polydispersity of the resins under investigation through evaluation of the angle of inclination of the straight line, this inclination increasing with the heterogeneity of the molecular mass.

Analysis of the relationships presented graphically makes it possible to evaluate the dispersion of molecular mass from the shape and extent of the integral and differential curves and to define the percentage proportion of the

individual fractions in the mass of the resin. It is also possible to secure comparative data regarding the dispersion composition of molecular mass of resins coming from different production lots when the same technological parameters are maintained or when ones changed in a specified manner are used. The use of the method of least squares for the construction of the curves under discussion makes it possible to calculate their most probable course.

The method presented for determining the molecular mass of solid resins, based upon preparative fractionation and determination of the viscosity of solutions of isolated fractions, does not impose difficulties in carrying out the experimental part; on the other hand, it does become more complicated regarding the determination and interpretation particularly of large number of results. These difficulties may be eliminated by entrusting to computer centers the programming and calculating, which makes the course of investigations more efficient and relieves those who carry out the calculations of the burden.

The method may be utilized for checking on the repeatability of technological processes, of the optimum selection of raw materials, and above all in investigating the effect of the polydispersity of phthalic resins upon their exploitational properties.

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